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Original Article

ESTIMATING CALORIFIC VALUE OF BIODIESEL USING FREE FATTY ACID CHEMICAL COMPOSITION

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ABSTRACT

Biodiesel can be used as an alternative fuel in diesel engine without substantial hardware modification with or without blending with diesel. The physico chemical properties such as calorific value, viscosity, density, flash point, cetane number etc plays a vital role while designing a fuel systemfor compressing ignition engine utilizing biodiesel, diesel or biodiesel mix. The calorific value is a significant land by virtue of that energy content of a fuel could be determined. Biodiesel contains 10 to 12% oxygen by weight which leads to proportionally lower energy density and heating value compared to diesel. The calorific value of nine different non-edible seeds oil biodiesels were measured and correlated using free fatty acid chemical composition analysis. An attempt is made to develop mathematical equation relating calorific value and chemical composition. The estimated calorific value compared with the calorific values which have been measured. It establishes the normal dependence of calorific result on free fatty acid chemical composition.

KEYWORDS: Calorific Value, Free Fatty Acid, Chemical Composition & Biodiesel

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1. INTRODUCTION

Biodiesel as an alternate fuel of diesel is referred to as fatty acid methyl or ethyl esters from vegetable oils or animal fats. Among the most essential properties to describe a fuel is its energy material. The normal measure of r energy content of a fuel is its own heating value occasionally referred to as calorific value or heat of combustion . The heating value is accessed by the complete combustion of a unit amount of liquid or solid fuel in oxygen-bomb calorimeter under closely specified conditions. The Gross Heat of Combustion or Greater Heating Value is acquired by oxygen-bomb calorimeter process since the latent heat of moisture from the combustion products is regained. The heat value is among the most crucial properties of a fuel. Some investigators have tried to gauge the HHV of these vegetable oils by making use of their physiological properties like: saponification and potassium data. Some researchers have tried to estimate that the HHV of those vegetable oils by using their Fatty acids article. Some researchers tried to gauge the worthiness on the grounds of fuel properties of vegetable oils including its viscosity, density, cetane number, cloud and pour points, distillation range, flash point, ash content, sulfur content, and carbon contentacid value, etc [1].

Chemical and physical properties of biodiesel are affected by the structural characteristics of fatty acid for example with saturated , mono unsaturated and poly unsaturated fatty acids. Better comprehension of the construction - physical land connection in fatty acid esters is of special importance when picking vegetable oils

which will give desirable high quality with true understanding of the effect of molecular arrangement to the properties ascertained. [2]The purpose of this analysis is to gauge mathematical connections between calorific value and free fatty acid compound makeup.

2. LITERATURE REVIEW

Number of researchers attempted to determine calorific value of biodiesel fuel either using chemical composition or using physical properties.

Demirbas (1998) "established the relation for higher heating value using iodine value and saponification number of biodiesel HHVs=49.43-0.041(SN) + 0.015(IV)".

Where SN is saponification number and IV is iodine value.

Gerhard Knothe, (2005) "has concluded that structural features that influence the physical and fuel properties of a fatty ester molecule are chain length, degree of unsaturation and branching of the chain. Important fuel properties of biodiesel that are influenced by the fatty acid profile and in turn by the structural features of the various fatty esters are cetane number and ultimately exhaust emissions, heat of combustion, cold flow, oxidative stability, viscosity and lubricity".

Ayhan Demirbas (2007) "estimated mathematical relationship between higher heating value and viscosity, density or flash point of various biodiesel fuels HHV=0.4625VS+39.450. Where VS is viscosity**,** HHV=-0.0259DN+63.776 where DN=density, HHV=0.021FP+32.12 where FP is Flash Point"**A. A. Refaat (2009)** "reviewed the relationship between the chemical structure and physical properties such as cetane number, viscosity and oxidation stability of vegetable oil esters and engineering fatty acid profiles to optimize biodiesel fuel characteristics".

K. Sivaramakrishnan et.al. (2011) "determined correlation for higher heating value using viscosity, density and flash point of biodiesel HHV=0.4527v-0.0008ρ-0.0003FP+40.3667and observed that there is an excellent agreement between measured and estimated values".

WANG LI-bing et.al. (2012) "used ten measure trees as the potential raw material of biodiesel as samples and developed a triangular predication graph for biodiesel fuel properties mainly cetane number, oxidation stability and iodine number".

Luis et.al. "established the relation for higher heating value using molecular weight of fatty acid methyl ester and number of double bonds $\delta i=46.19-\frac{1794}{Mi}-0.21N$ where δi is higher heating value, Mi is molecular weight of ith fatty acid methyl ester and N is number of double bonds [24]".

Lai Fatt Chuah et.al. (2015) "selected seven non edible oils for predicting the properties of biodiesel. cetane number, oxidation stability and iodine value were correlated with degree of unsaturation of fatty acid. Cold filter plugging point was correlated with long chain saturation factor".

3. MATERIALS AND METHODS

For analysis purpose nine different non-edible vegetable oil seeds have been selected as given in table below:

Table 1

S No.	Common Name	Botanical Name
1	Ratan jyot	Jatropha curcas
2	Karanja	Pongamia pinnata
3	Mahua	Madhuca indica
4	Babul	Acacia Radiana
5	Muskmelon	Cucumis melo
6	Awala	Phyllanthus emblica
7	Jamun	Syzygium cumini
8	Milo	Thespesia populnea
9	Castor	Ricinus communis

3.1 Oil Extraction Process

A variety of methods like mechanical extraction, solvent extraction, conventional extraction and super critical fluid extraction have been utilized to acquire the oil in the seeds. The solvent extraction is now the most popular technique of extraction of oil due to its high proportion of petroleum recovery in seeds. Solvent extraction bridges the difference between mechanical extraction that produces oil with higher turbidity alloy and water material along with super critical fluid extraction that's quite costly to construct and maintain its own facilities. Temperature is raised for oil seeds following pre treatments like cracking, decupling and milling by warmth, roasting and ingestion of oil seeds before extraction and can be called as thermal therapy of oil seeds. Better extraction is accomplished by heating system, which decreases the oil viscosity and discharged oil from undamaged cells, and also reduces moisture from the cells. Infection has an active part in the seed therapy for mechanical extraction also ensures a successful purification procedure by heating the effluent that has tens the extraction procedure. In the ideal temperature and moisture content, the oil droplets s combine to make a constant phase and stream out optimizing oil return. Solvent extraction is that the usage of substances as solvents in the extraction of oil from oil seeds. Solvent extraction is well known for its high oil producing output, ease and swiftness to execute: comparatively economical, higher over head cost and also toxic impacts . The usage of the process demands a comprehensive refining procedure to guarantee traces of these solvents to be eliminated completely. Solvent extraction of cracked, dehulled and skillet with hexane is commercially practiced to extract petroleum. [3]

3.2 Gas Chromatography

Gas chromatography (GC) is a frequent sort of chromatography employed in analytic chemistry to get dividing and assessing substances which could be vaporized with no decomposition. Normal applications of GC comprise analyzing the innocence of a specific material, or dividing the various constituents of a mix (the comparative amounts of these elements may likewise be as curtained). In certain scenarios, GC might aid in identifying a chemical. At preparative chromatography, GC may be employed to prepare pure substances from a mix. [4][5]

In gas chromatography, the mobile phase (or even “transferring stage") is a carrier gas, generally an inert gas like helium or an unreactive gas like nitrogen. Helium stays the most widely used carrier gas in roughly 90 percent of devices though hydrogen is favored for enhanced separations. The stationary phase is a microscopic coating of liquid or plastic within an inert strong support, either within a object of glass or metallic tubing known as a column.

The gaseous materials being examined socialize with the walls of this pillar, which can be coated with a stationary phase. This causes each chemical into elute in another time, called the retention period of this chemical. The significance

of retention times is that which provides GC its analytical utility. [6]

3.3 Biodiesel Production

Generally two phase transesterification procedure is employed for the creation of biodiesel. This procedure is made up of sequence of three successive reversible response i.e. conversion of triglycerides into diglycerides accompanied by diglycerides into mono glyceride. The glycerides were transformed to glycerol and a single ester molecule at every step. In this event the oil contains over 4 percent free fatty acids (FFA), then two step transesterification is related to convert the large FFA oils into its own mono esters. Step one the acid catalyzed esterification lessens the free fatty acid content of the oil.

$$\text{Vegetable oil} + \text{Alcohol} \overset{\text{acid}}{\rightleftharpoons} \text{Triglyceride} + \text{water}$$

The next step, alkaline transesterification procedure converts the goods of this very first step to the mono-esters along with glycerol. Inside this procedure vegetable oils are heated to temperatures of 80^0 C -85^0 C by putting in water tub. Likewise alcohol is warmed to 65^0C at the presence of alkali catalyst. Both vegetable oil and alcohol are all blended together in a fever of 60^0C -65^0C . The response leads to the creation of esters and glyceride water has been blended to the mix, soap is going to be formed that lessens the creation of biodiesel. The chemical reaction is

$$\text{Triglyceride} + \text{alcohol} \overset{\text{alkali}}{\rightleftharpoons} \text{Glycerol+alkyl esters}$$

Simple alcohols are utilized for transesterification and this procedure is generally carried out using a fundamental catalyst (NaOH, KOH) from the entire lack of plain water. Too much alcohol is required to accelerate the response. Together with methyl, alcohol glycerol fracture occurs easily. From the transesterification process, alcohol unites with the entire molecule out of acid to make glycerol and ester. The glycerol is subsequently eliminated by density separation. Transesterification reduces the viscosity of oil, which makes it closer to diesel fuel in features. [7]

3.4 Measuring Gross Calorific Value

Gross calorific value of a gas is that the energy realized by burning unit quantity of fuel if products of combustion are cooled to atmospheric conditions. It provides the energy content at a fuel. The gross calorific value of biodiesel was quantified in a bomb calorimeter based on ASTM D240 regular system. Heat of combustion will be decided in this evaluation process by burning off a weighed sample in an oxygen bomb calorimeter under regulated conditions. Together with the evaluation sample and fuse set up, gradually charge the bomb with oxygen to 30 bar gauge pressure at room temperature.The heat of combustion can be calculated from temperature observations prior to, during, and after combustion, with appropriate allowance for thermo chemical and heat transport corrections.

4. RESULTS & DISCUSSIONS

4.1 Free Fatty Acid Chemical Composition[8][11][12][14][15][16][17][18][23]

Nine different seeds oil have been selected for analysis purpose. Free fatty acid chemical analysis of vegetable oils is taken from published data .

Table 2

S No.	Seed oil Biodiesel	Stearic Acid % C18:0	Palmitic Acid % C16:0	Lignoceric Acid % C24:0	Myristic Acid % C14:0	Oleic Acid % C18:1	Recinoleic Acid % C18:1(O)	Linoleic Acid % C18:2	Linolenic Acid % C18:3
1	Jatropha	8.6	13			45.4		33	
2	Karanja	7.5	7.9	4		51.59		28.9	
3	Mahua	22	22	2		43		11	
4	AcaciaRadiana	6.5	38			34.5		21	
5	Cucumis melo	10.84	17.68			21.12		50.4	
6	Awala	7.1	9			30.1		44	9.8
7	Jamun	7.5	4.7	2.8	28.9	36.2		16.7	3.2
8	Milo	7.3	26.8		3.6	19.1		39.2	4
9	Castor	1	1.7			2.28	87.22	4.3	3.5

4.2 Linear Least Square Regression Analysis

Chemically the seeds oil consists of various free fatty acids which can be categorized in to three main types i.e. saturated, mono unsaturated and polyunsaturated. [28] The calorific value is considered as a function of chemical composition. An equation is developed for calorific value of seed oil bio diesel using chemical composition with the help of linear least Square Regression Analysis. While selecting nine seeds care has been that each category is having three seeds in which corresponding percentage is larger.

Calorific value = $(K_1 \times S) + (K_2 \times M) + (K_3 \times P) + K_4$

Where K_1, K_2, K_3, K_4 are constants S, M and P stands for percentage of saturation, mono unsaturation and poly unsaturation respectively

Table 3

Sr. No.	Seed Oil Biodiesel	Measured CVMJ/Kg	Poly Unsaturation%	Mono Unsaturation %	Saturation %
1	Jatropha	40	33	45.4	21.6
2	Karanja	39	28.9	51.6	19.5
3	Mahua	36	11	43	46
4	Acacia Radiana	35.78	21	34.5	44.5
5	Cucumis melo	46	50.4	21.1	28.5
6	Awala	47	53.8	30.1	16.1
7	Jamun	39	19.87	36.2	43.93
8	Milo	43.1	43.2	19.1	37.7
9	Castor	37.2	7.8	89.5	2.7

$y=ax+b$

$a\sum x+Nb= \sum y$

$a\sum x^2+ b \sum x = \sum xy$

By using above for each category three equations have been developed

For Poly unsaturation,

$$CV = 0.2341\% \, P + 33.90 \tag{1}$$

For Mono unsaturation,

$$CV = -\ 0.108\%\ M + 44.79 \quad (2)$$

For Saturation,

$$CV = -\ 0.072\%\ S + 42.43 \quad (3)$$

Hence, $K_1 = -0.072$

$K_2 = -0.108$

$K_3 = 0.2341$

$K_4 = 40.37$

Therefore Calorific Value = - 0.072%S - 0.108%M + 0.2341%P + 40.37

4.3 Determination of Correlation Coefficient

Table 4

Sr. No.	Seed Oil Biodiesel	Measured CV (y)	Calculated CV (x)	Absolute Error	% Error
1	Jatropha	40	41.64	1.64	4.09
2	Karanja	39	40.16	1.16	2.97
3	Mahua	36	34.99	1.01	2.81
4	Acacia Radiana	35.78	38.36	2.58	7.20
5	Cucumis melo	46	47.84	1.84	4.00
6	Awala	47	48.55	1.55	3.31
7	Jamun	39	37.95	1.05	2.69
8	Milo	43.1	45.71	2.61	6.05
9	Castor	37.2	36.92	0.28	0.77

$$\text{Correlation Coefficient I} = \frac{\sum xy - N\bar{x}\,\bar{y}}{\sqrt{(\sum x^2 - N\,\bar{x}\,\bar{x})(\sum y^2 - N\,\bar{y}\,\bar{y})}}$$

Where,

$\bar{x} = 41.35$

$\bar{y} = 40.34$

$\sum xy = 15169.44$

$\sum x^2 = 15579.68$, $\sum y^2 = 14784.66$

$R = 0.9693$, $R^2 = 0.9395$

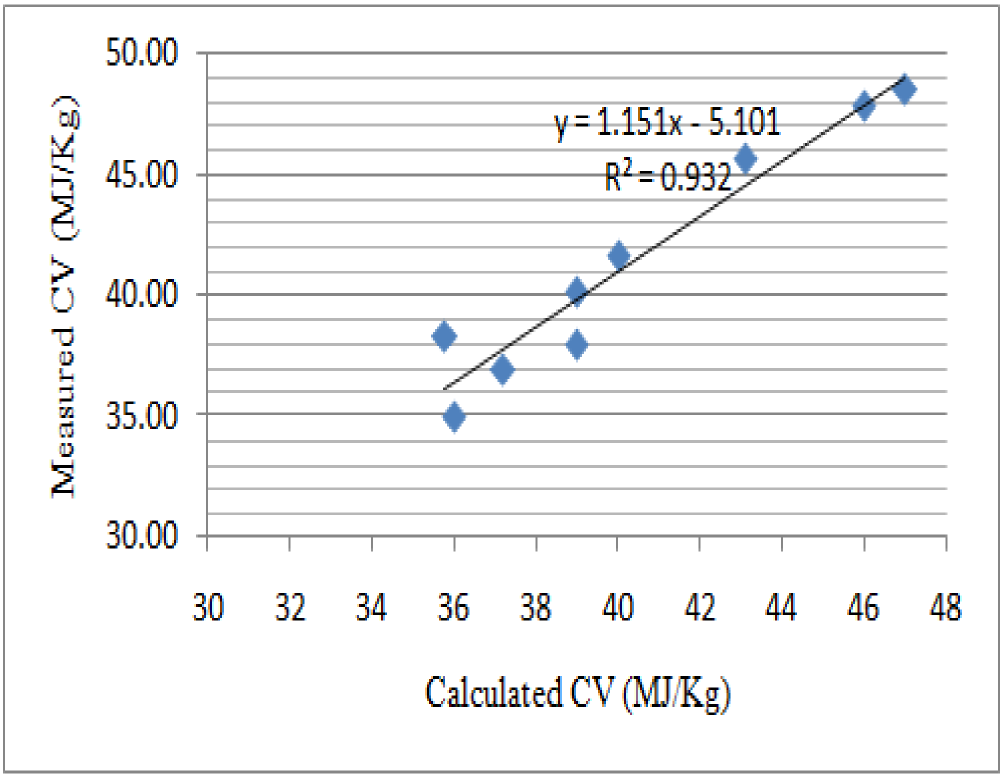

Figure 1

4.4 Correlation Coefficient for Calorific Value Based on Poly Unsaturation

Calorific value is calculated using equation for calorific value based on polyunsaturation i.e.

CV = 0.2341% P + 33.9

Table 5

Sr. No.	Seed Oil Biodiesel	Measured CV (y)	Calculated CV (x)	Absolute Error	% Error
1	Jatropha	40	41.6253	1.6253	4.06325
2	Karanja	39	40.6655	1.66549	4.27049
3	Mahua	36	36.4751	0.4751	1.31972
4	Acacia Radiana	35.78	38.8161	3.0361	8.48547
5	Cucumis melo	46	45.6986	0.30136	0.65513
6	Awala	47	46.4946	0.50542	1.07536
7	Jamun	39	38.5516	0.44843	1.14983
8	Milo	43.1	44.0131	0.91312	2.11861
9	Castor	37.2	38.5305	1.3305	3.57661

Correlation Coefficient (R) = $\frac{\sum xy - N\bar{x}\,\bar{y}}{\sqrt{(\sum x^2 - N\,\bar{x}\,\bar{x})(\sum y^2 - N\,\bar{y}\,\bar{y})}}$

Where, $\bar{x} = 41.20$

$\bar{y}$ = 40.34

$\sum xy = 15072.45$

$\sum x^2 = 15378.16$, $\sum y^2 = 14784.66$

$R = 0.9766$

$R^2 = 0.9537$

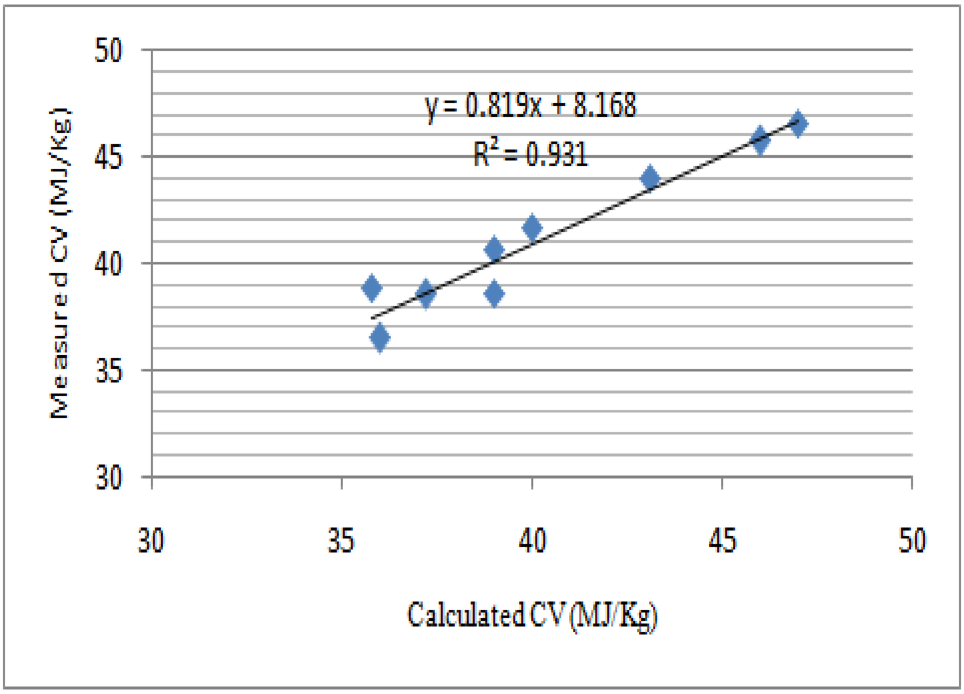

Figure 2

5. CONCLUSIONS

A new method for estimation of calorific value of biodiesel is developed. The intention of this task is to demonstrate that it is possible to estimate the calorific value of seeds oil biodiesel from their chemical composition comprising of various free fatty acids categorized in to three groups that is saturated, mono unsaturated and polyunsaturated. An equation is developed to estimate calorific value based on chemical composition using 0.939 accuracy. The developed equation could efficiently forecast the calorific value of biodiesel. There's a great agreement between estimated and measured values.

6. FUTURE SCOPE

Similar to calorific value we can estimate other biodiesel fuel properties such have density, viscosity, flash point, cloud and pour point, cetane number etc using free fatty acid chemical composition.

7. ACKNOWLEDGEMENT

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